

New copolymerizable photoinitiators for radiation curing of acrylic PSA

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ABSTRACT

This article presents a new class of copolymerizable photoinitiators containing vinyloxy carbonyl groups, known such as organic carbonate or carbamate. Novel copolymerizable photoinitiators have been prepared through the reaction between vinyl chloroacetate and hydroxyl groups containing photoreactive derivatives such as benzophenone, acetophenone, benzoin- and anthracinone-derivatives. The main emphasis is given to the influence of this new class of unsaturated photoinitiators on UV-crosslinking process of acrylic pressure-sensitive adhesives (PSA). Moreover, the paper describes the influence of various parameters such as UV-initiated crosslinking time and concentration of unsaturated photoinitiators on relevant PSA properties like tack, peel adhesion and shear strength (cohesion).

Keywords: copolymerizable photoinitiators; UV-crosslinking; pressure-sensitive adhesive (PSA); acrylics; tack; peel adhesion; shear strength

1. INTRODUCTION

UV-induced crosslinking is a rapidly expanding technology on pressure-sensitive adhesives area resulting from its main advantages such as solvent-free process, efficient and economical energy used and final properties and quality of chemical crosslinking bonding [1]. This photocrosslinking process found interesting application for producing photoreactive PSA systems used in the coating industry for paints, printing, inks, dental materials, adhesives and self-adhesive tapes.

The idea of replacing the conventional two-part thermally crosslinked systems with single-component room temperature photoactivated pressure-sensitive adhesives became very attractive for manufacturing industries [2-5].

The basic principle of UV crosslinking pressure-sensitive adhesives is the conversion of UV energy into chemical energy. This energy conversion takes place through the use of chemical species (photoinitiators) which, upon absorption of a particular wavelength of light, produce photochemically reactive radicals capable of initiating a rapid chain reaction. With the use of commonly available light sources it can be calculated that as many as 10^{19} initiating photoinitiators per second can be generated. It is therefore not surprising that the radiation crosslinking systems on the market today can be crosslinked so rapidly that it is sometimes in less than one second [6].

The most important features of the crosslinked acrylic pressure-sensitive adhesives, such as tack, peel adhesion and shear strength can be controlled by the UV dosage. The crosslinking of PSA with ultraviolet radiation can be done directly after the application.

The crosslinking mechanism of UV photoreactive acrylics PSA containing copolymerizable photoinitiators has been thoroughly investigated and it is presented schematically (Fig. 1) [7-10].

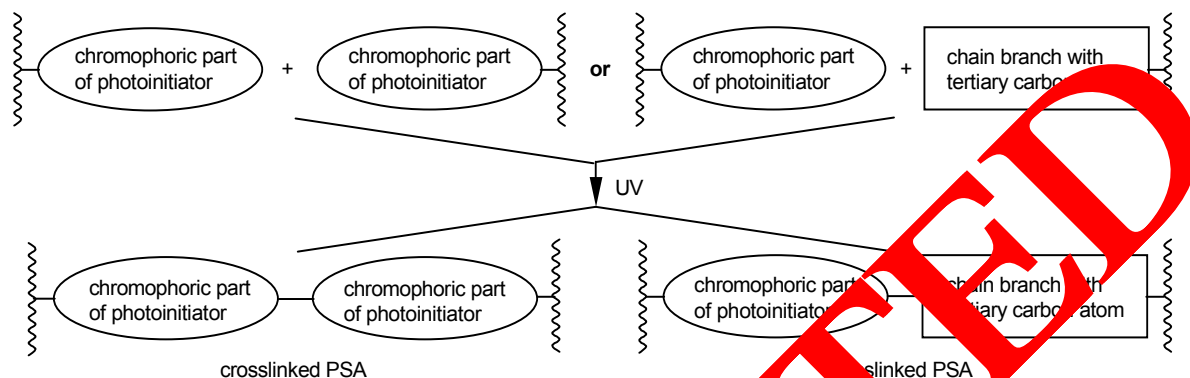


Figure 1. Photocrosslinking by using of unsaturated photoinitiators incorporated into polymer chain.

During UV exposition the intermolecular photoinitiator H-abstractors structures are excited and react with the neighbouring C-H positions of polymer side-chains. UV-crosslinkable acrylic pressure-sensitive adhesives possess excellent oxidation resistance which allows working without inert gas atmosphere [1].

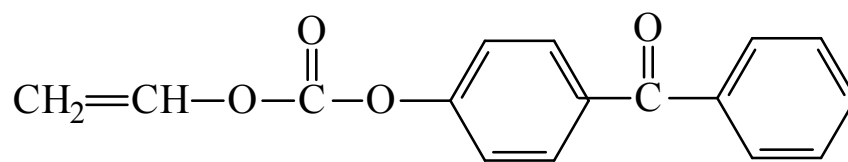
2. EXPERIMENTAL

2. 1. Materials

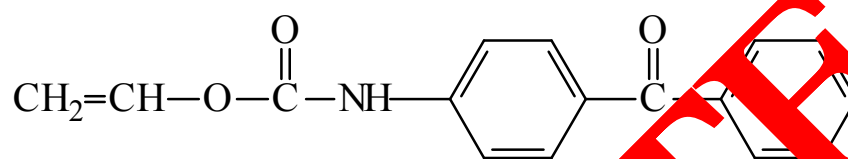
The following experiments were conducted to study the influence of a new class of copolymerizable photoinitiators on diverse main acrylic PSA properties, such as: viscosity, molar mass, tack, peel adhesion, and shear strength. The acrylic PSAs were synthesized using between 62 and 64,5 wt. % (step 0.5 wt. %) 2-ethylhexyl acrylate (2-EHA), 30 wt. % methyl acrylate (MA), 5 wt. % acrylic acid (AA) and between 0.5 and 3 wt. % (step 0.5 wt. %) investigated copolymerizable photoinitiators during polymerization in a typical organic solvent like methyl acetate with polymer content of 50 % by weight [12, 13].

2-ethylhexyl acrylate (2-EHA), methyl acrylate (MA), acrylic acid (AA) and ethyl acetate were available from Poly-Chem (Germany).

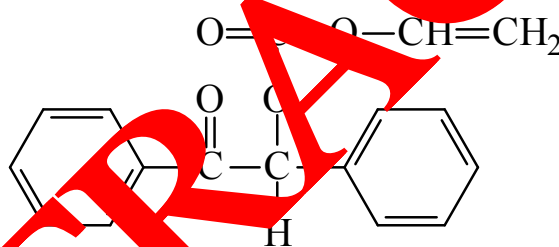
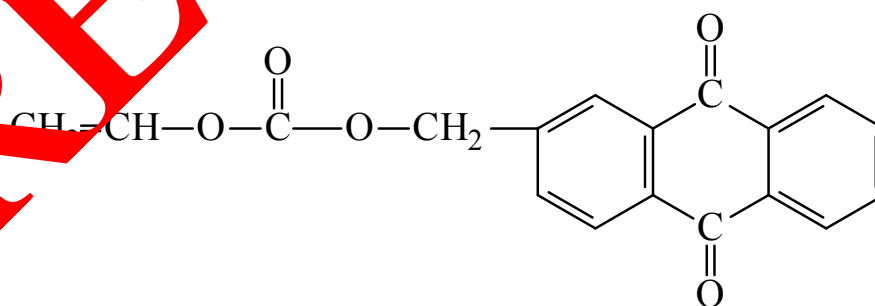
The copolymerizable photoinitiators (α -cleavage type I and hydrogen abstraction type II) were synthesized at Szczecin University of Technology (Poland) through the reaction between vinyl chloroformate and hydroxyl groups containing photoreactive derivatives. The following copolymerizable photoinitiators (Fig. 2) have been prepared according [11].



4-Benzophenylvinyl carbonate (hydrogen abstraction type II)



4-Benzophenylvinyl carbamate (hydrogen abstraction type II)

Vinyl oxycarbonylbenzoin ether (α -cleavage type I)

2-Vinyloxycarbonyloxymethyl anthracinone (hydrogen abstraction type II)

Figure 2. New class of investigated copolymerizable photoinitiators.

2. 2. Evaluation of PSA properties

Tack, peel adhesion and shear strength of investigated photoreactive acrylic pressure-sensitive adhesives were measured according to AFERA 4015 (tack), 4001 (peel adhesion) and 4012 (shear strength).

The UV-crosslinkable acrylic PSA were coated with 60 g/m² coating weight directly on a polyester foil and later after drying crosslinked under UV lamp of type U 350-M-I-DL from IST Company (Germany). The resulted samples were cut into one-inch strips and applied to stainless steel. The tack, peel adhesion and shear strength were measured on Zwick testing machine after a specified 1 week dwell period.

2. 3. UV-absorption of investigated photoinitiators

The UV-absorption curves of investigated copolymerizable photoinitiators were conducted using Hewlett Packard Diode Array UV/VIS Spectrophotometer and shown in Figure 3.

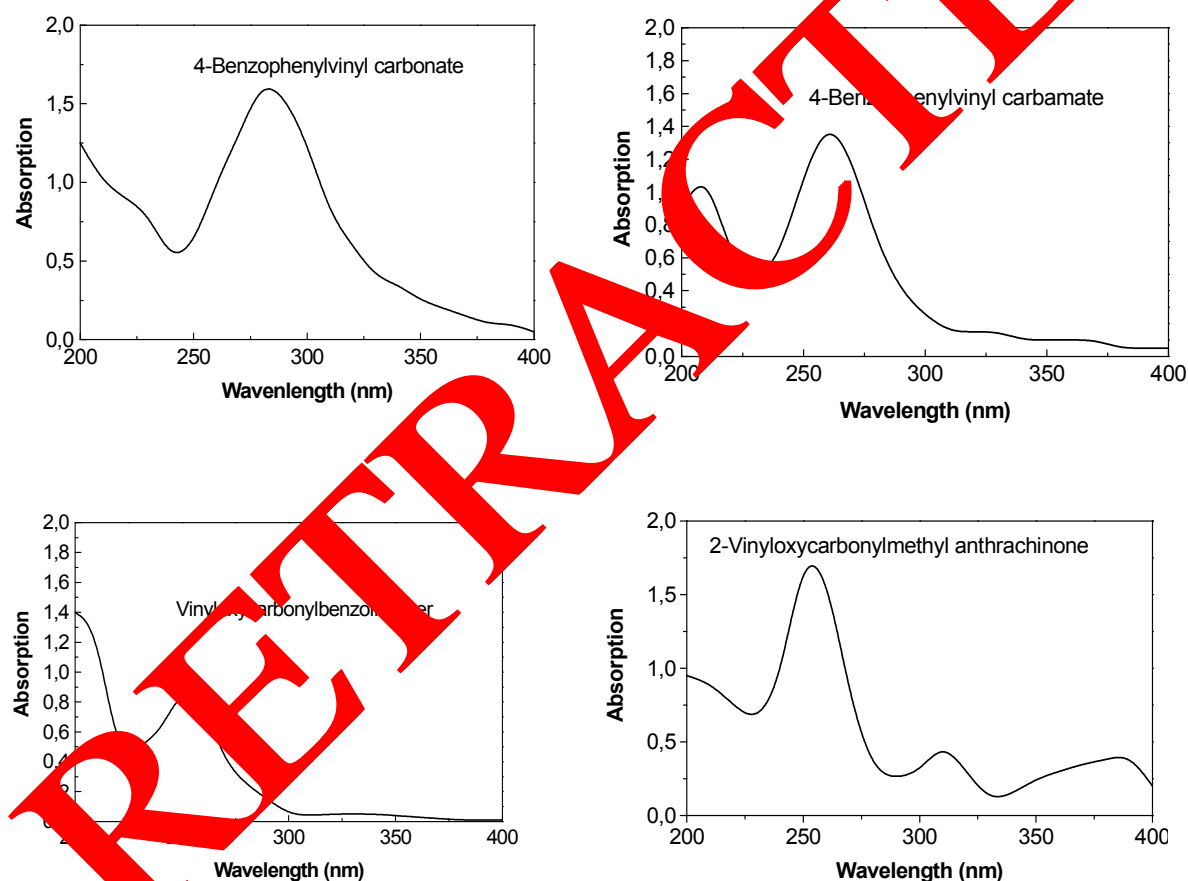


Figure 3. UV-absorption curves of investigated copolymerizable photoinitiators.

The UV-absorption curve of 4-benzophenylvinyl carbonate shows strong absorption at 280 nm, of 4-benzophenylvinyl carbamate at 263 nm, of vinyloxycarbonylbenzoine ether at 255 nm and of 2-vinyloxycarbonyloxymethyl anthracinone at 256, 317 and at 387 nm which are also very compatible with the output lines from a medium-pressure mercury lamp commonly used for crosslinking systems of this type.

3. RESULTS AND DISCUSSION

3. 1. Effect of copolymerizable photoinitiators on viscosity

The solvent-based acrylic PSAs were synthesized with diverse concentrations of investigated copolymerizable photoinitiators from 0.5 to 3.0 wt. %. The viscosities of synthesized acrylic PSAs are presented in Fig. 4.

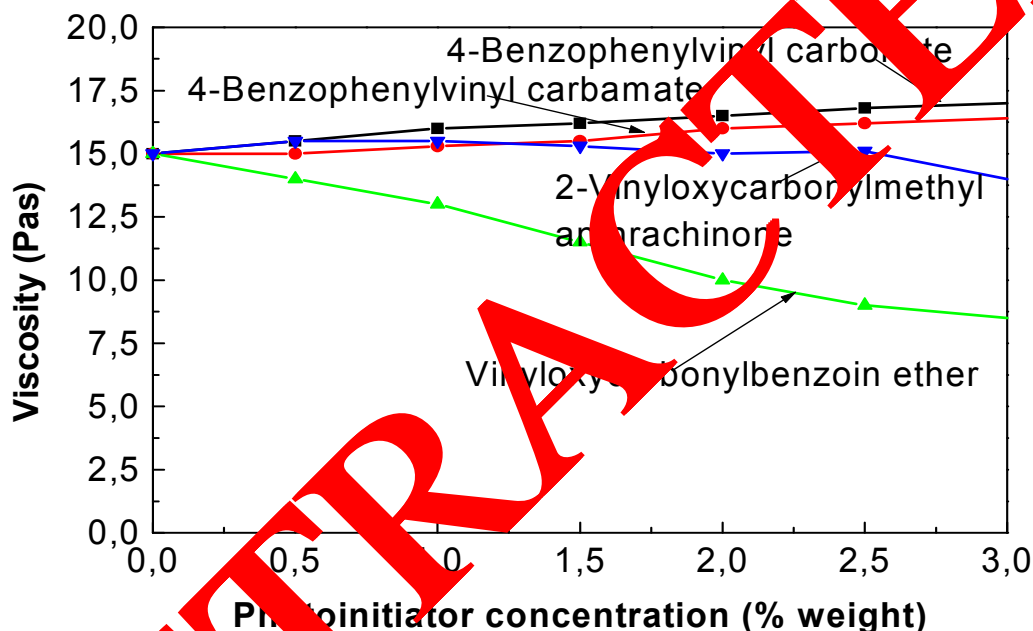


Figure 4. Influence of photoinitiator concentration on viscosity of synthesized PSAs.

As expected, the copolymerisation of photoinitiators: 4-benzophenylvinyl carbonate, 4-benzophenylvinyl carbamate and 2-vinyloxycarbonyloxymethyl anthracinone influences positively the viscosity of synthesized pressure-sensitive adhesives. Only application of photoinitiator vinyloxycarbonyl-benzoine ether influences the viscosity of solvent based PSA negatively.

3. 2. Influence of copolymerizable photoinitiators on molecular mass

The results of the influence of the investigated copolymerizable photoinitiators on molecular mass of solvent-based synthesized acrylic PSAs are presented in Fig. 5.

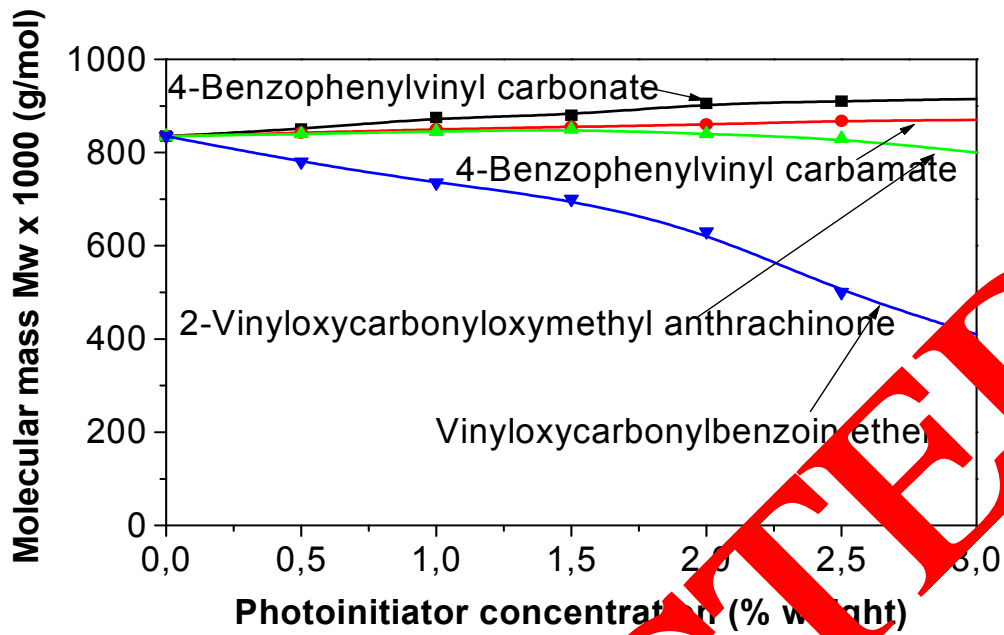


Figure 5. Effect of photoinitiator concentration on molecular mass of synthesized PSAs.

3. 3. Influence of the photoinitiators concentration on tack of synthesized PSAs

The solvent-based pressure-sensitive adhesives were coated on polyester foil with coat weight of 60 g/m² and crosslinked under coating 30 s under UV-lamp. The results of tack, peel adhesion and shear strength were showed in Figs. 6-8.

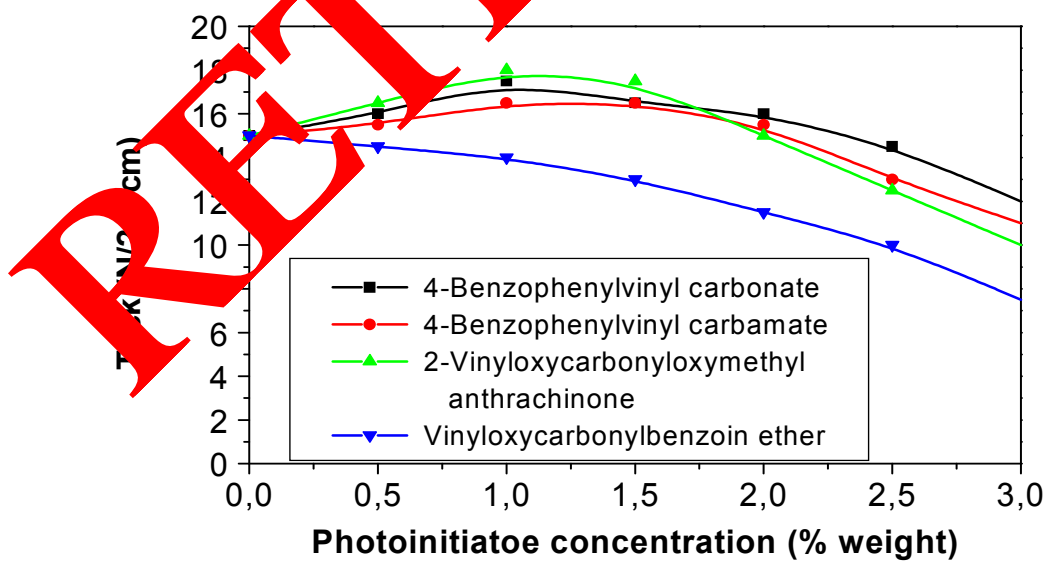


Figure 6. Tack of synthesized PSAs dependent on photoinitiator concentration.

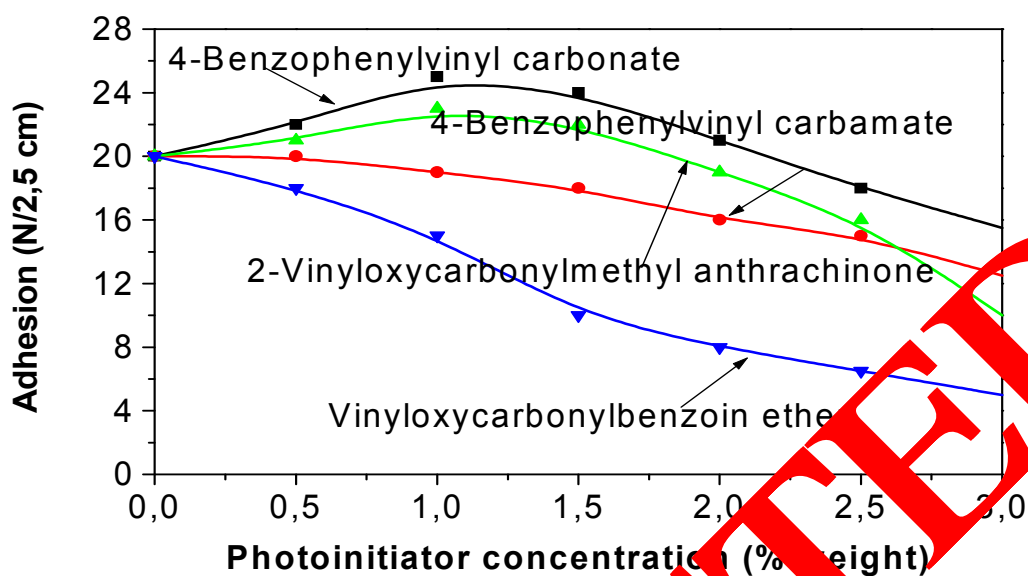


Figure 7. Peel adhesion of synthesized PSAs dependent on photoinitiator concentration.

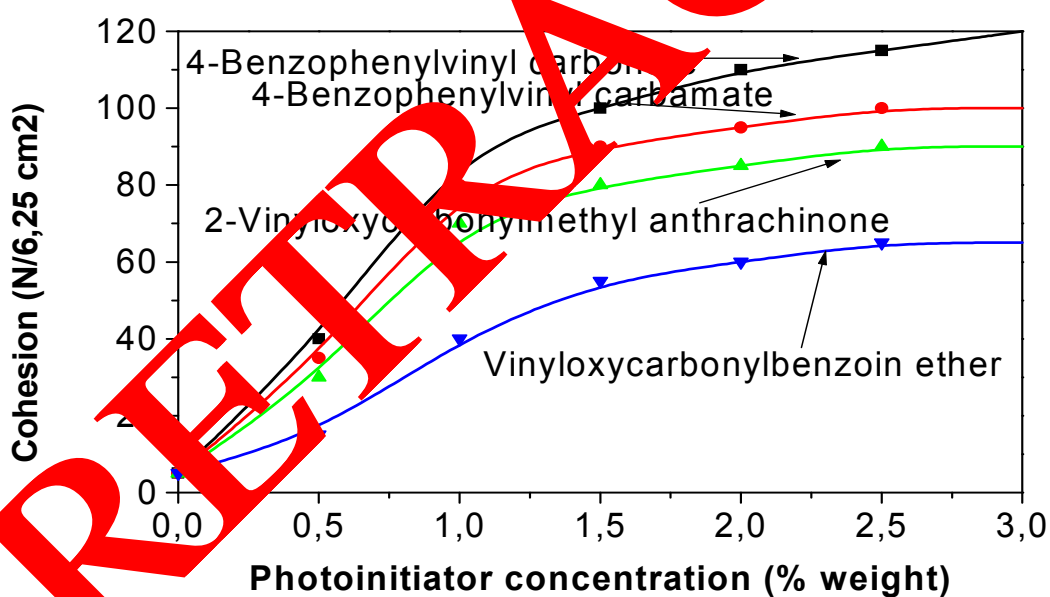


Figure 8. Shear strength of synthesized PSAs dependent on photoinitiator concentration.

The investigation of the influence of photoinitiator concentration on tack in case of UV-crosslinking of photoreactive acrylic pressure-sensitive adhesives enables it to be observed that the most efficient photoinitiator is 4-benzophenylvinyl carbonate. The highest value of tack was obtained by using of 1 wt. % of this photoinitiator. The remaining two

photoinitiators 4-benzophenylvinyl carbamate and 2-vinyloxycarbonyloxymethyl anthracinone are not effective so much. The definitely least effective photoinitiator appeared vinyloxycarbonylbenzoine ether (Fig. 6).

4-benzophenylvinyl carbonate appeared also to be the most effective photoinitiator as to the investigated peel adhesion of the UV crosslinking acrylic pressure-sensitive adhesives. A maximal adhesion was noticed for the concentration of 1 wt. % 4-benzophenylvinyl carbonate. Lower values of peel adhesion were received in case of the photoinitiators: 4-benzophenylvinyl carbamate and 2-vinyloxycarbonyloxymethyl anthracinone. Vinyloxycarbonylbenzoine ether was evidently the lowest effective photoinitiator.

The increase of the concentration of unsaturated photoinitiators in synthesized acrylic PSAs causes in general an increase of shear strength in the resulting adhesives. A high cohesion value of 90 N order of magnitude was possible to be obtained already by applying 1 wt. % 4-benzophenylvinyl carbonate. Further increasing the concentration of this photoinitiator enables to increase shear strength up to 120 N. 4-benzophenylvinyl carbonate and 2-vinyloxycarbonyloxymethyl anthracinone are a bit less effective than 4-benzophenylvinyl carbonate. Vinyloxycarbonylbenzoine ether proved also to be one of the least effective photoinitiators, shear strength of 40 N being obtained to be one of the least effective photoinitiators, shear strength of 40 N being attained for the 1.5wt. % concentration and shear strength of about 60 N being achieved on further increasing the photoinitiator concentration.

4. CONCLUSIONS

From the evaluation of the experiments discussed in this article, it can be concluded that all the investigated copolymerizable photoinitiators can be used for polymerization and after polymerization to UV-initiated crosslinking of pressure sensitive adhesive acrylics. The UV-absorption curves of copolymerizable photoinitiators shows strong absorption in areas of typical UV lamps and can be used for UV-crosslinking of photoreactive acrylic PSA system. Generally 4-benzophenylvinyl carbonate, 4-benzophenylvinyl carbamate and 2-vinyloxycarbonyloxymethyl anthracinone influences very little the viscosity of solvent based pressure sensitive adhesive. Vinyloxycarbonylbenzoine ether decreases the viscosity of acrylic PSAs. The similar effect was observed for the influence of molecular mass of synthesized self adhesive acrylics.

From the investigated copolymerizable photoinitiators, the best results for relevant properties of pressure sensitive adhesives such as tack, peel adhesion and shear strength were given by 4-benzophenylvinyl carbonate. The highest values of tack, peel adhesion and shear strength were observed at concentration about 1 % by weight of 4-benzophenylvinyl carbonate. The properties of synthesized PSA containing 4-benzophenylvinyl carbonate are after UV crosslinking excellent. The shear strength shows very high level.

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